III.B.6 Operation of Solid Oxide Fuel Cell Anodes with Practical Hydrocarbon Fuels

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Objectives

- This work was carried out to achieve a better understanding of how solid oxide fuel cell (SOFC) anodes work directly with hydrocarbon fuels, examining both basic mechanisms and feasibility of this approach for SOFC stacks.
- Another objective was to use the basic information on hydrocarbon-anode reactions to better understand how SOFCs work with partially reformed fuel gas that contains residual hydrocarbons.
- Since real fuels contain sulfur, one goal was to examine the effects of sulfur on SOFC performance.
- The work also aimed to further develop not only Ni-YSZ (yttria-stabilized zirconia) anodes, but also ceramic-based anode compositions.

Approach

- SOFCs were fabricated using conventional ceramic processing methods, with both conventional Ni-YSZ anodes and novel ceramic anodes.
- Structural and chemical measurements of SOFC anodes were carried out in order to verify anode structure and composition and to detect coking.
- Differentially-pumped mass spectrometry was used for product-gas analysis, both with and without cell operation.
- Impedance spectroscopy was used in order to understand electrochemical rate-limiting steps.
- Life tests over a wide range of conditions were used to establish the conditions for stable operation or coking of anode-supported SOFC stacks directly on methane.
- Redox cycling was carried out on ceramic-based anodes.
- Tests on sulfur tolerance of Ni-YSZ anodes were carried out.
- The results from the various measurements above were analyzed together to obtain a more complete picture of fuel-anode interactions.

Accomplishments

- Direct methane power densities as high as 0.5 W/cm^2 at 700°C and 1.25 W/cm^2 at 800°C have been achieved. It is clear that further improvements are possible.
- Good fits to the open circuit voltage (OCV) data for various fuel compositions were obtained based on equilibrium calculations.

- Electrochemical impedance spectroscopy (EIS) measurements carried out during SOFC operation suggested that anode polarization was substantially larger for methane than for hydrogen. These results indicate that gas diffusion in the anode support played an important role in determining cell performance.
- Mass spectrometer measurements showed that the expected reaction products – H_2, H_2O, CO, and CO_2 – all increased with increasing cell current density. The dominant products at 800°C were H_2 and CO, in agreement with thermodynamic predictions. However, the thermodynamic predictions could not directly explain the lack of coking during direct methane operation.
- We have mapped out the stability region for direct methane operation. At lower temperatures, ≤700°C, stable operation without coking occurs over a wide range of current densities, whereas at higher temperatures, increasingly large currents are required to avoid coking and cell failure.
- A much wider stability range was achieved using fuel gases containing diluted methane such as would be present in partially reformed methane.
- Degradation of cell performance was observed for H_2S-contamined H_2 fuel at 800°C, but surprisingly, the degradation was negligible at 700°C.
- Ceramic-based anodes showed good fuel flexibility with hydrogen, methane, ethane, propane, and butane, and excellent cell stability in redox cycling with hydrogen-air and propane-air.

Future Directions

No additional work is planned, but open issues include:

- Further work is needed to more fully characterize the S poisoning effects observed and to develop ways to minimize these effects.
- Further work is needed to develop detailed models of methane interactions, particularly diffusion and reaction processes within SOFC anodes.
- The present results have suggested new means for improving the stability of Ni-YSZ anodes in hydrocarbon fuels – these should be pursued.
- The direct methane SOFC should be studied as a means for low-cost, high-efficiency production of hydrogen by electrochemical partial oxidation.
- Ceramic anodes should be implemented in anode- or cathode-supported cells in order to verify that high power densities and stable operation can be achieved.

Introduction

Fuel cell power plants have been successfully demonstrated many times, but the high cost of these systems has prevented commercialization. One of the key factors that contribute to this high cost is a lack of fuel flexibility. Fuel cells generally operate only on hydrogen, which is neither readily available nor easily stored. Ideally, fuel cells should be able to utilize conventional hydrocarbon fuels ranging from natural gas to propane to gasoline. To utilize hydrocarbons, fuel cell power plants usually employ fuel reforming, which converts fuels into hydrogen that can be used directly. Reforming and exhaust-gas recirculation (which provides the steam for reforming) lead to additional plant complexity and volume, increasing cost. Real fuels also contain sulfur contaminants that typically poison fuel cell anodes, decreasing performance. Thus, adsorbents must be used to remove the sulfur, and the adsorbent materials must be changed or regenerated after they become saturated. Based on the above arguments, fuel cell system cost could be substantially reduced if the fuel cells themselves could operate directly on real fuels.

Recent reports have described SOFC operation directly on methane and natural gas. These results have challenged traditional views that large amounts of steam are required to prevent carbon deposition on Ni-containing anodes. Heavier hydrocarbons such as propane, butane, and even gasoline have been used

directly in SOFCs[1,2], although it was necessary in this case to utilize alternate anode compositions, replacing the Ni with either Cu or a conducting ceramic. Prior to this study, there had been little attempt to understand the mechanisms whereby direct-hydrocarbon SOFCs operate.

Approach

In the Phase I project, we have studied the reaction mechanisms of hydrocarbons on two kinds of anodes: conventional Ni-based anodes and ceramic-based anodes. The effects of sulfur impurities and of redox cycling were also considered. The project was aimed both at achieving an understanding of the interactions between real fuels and SOFC anodes, and at providing information required to operate SOFCs directly on hydrocarbon fuels. In particular, we have carried out detailed studies of the operation of Ni-YSZ anodes in methane-containing fuels, including cell tests, impedance spectroscopy, mass spectrometric studies of anode exhaust gas, studies of open circuit voltages, studies of the addition of H_2S to the fuel, and lifetime studies designed to determine useful direct-methane operating conditions. In addition, new ceramic-based anodes have been developed that provide good performance without coking with a range of hydrocarbon fuels and are also extremely tolerant of redox cycling.

Results

Extremely good performance was achieved for direct-methane SOFCs. Figure 1 shows typical voltage and power density vs. current density of a SOFC operated on methane. The maximum power density was 1.25 W/cm^2 at 800°C. Note that operation in methane was not stable under some conditions, especially high *T* and low *J*; this is discussed further below. The open circuit voltage (OCV) in methane increased with increasing temperature, opposite of the usual trend shown for hydrogen. This trend agrees reasonably well with the OCV predicted based on the equilibrium anode gas composition.

Gd-doped ceria (GDC) electrolyte cells with $(La,Sr)(Cr,V)O_3$-GDC anodes were operated in various fuels. Power densities were lower than

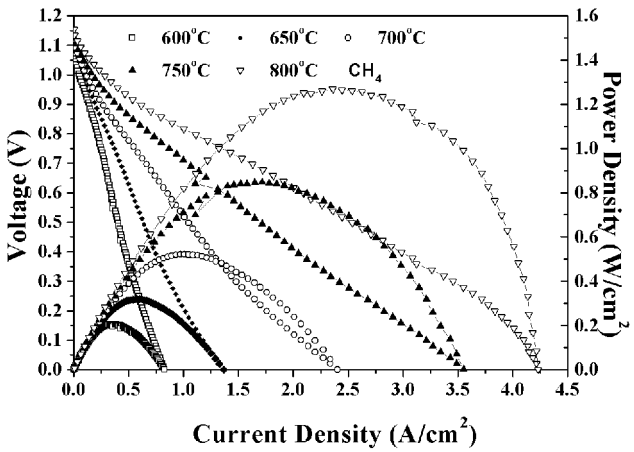
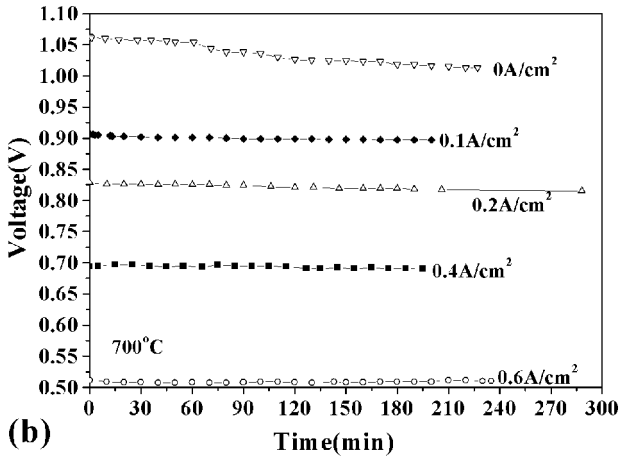


Figure 1. Voltage and Power Density vs. Current Density of a SOFC Operated on Humidified Methane

shown in Figure 1; e.g., with propane fuel the values were 120 mW/cm^2 at 650°C and 150 mW/cm^2 at 750°C. However, the low values were primarily due to the high resistance of the thick GDC electrolyte, and a more detailed analysis indicates that these electrodes have low enough resistances to allow much higher power densities. The cells were also successfully operated with hydrogen, methane, ethane, propane, and butane fuels at 700°C with similar power densities. Note that similar results have been obtained in cells with doped $SrTiO_3$-based anodes.

Electrochemical impedance spectroscopy (EIS) measurements were also done. The first real-axis intercepts, at 0.26 Ωcm^2 (600°C) and 0.10 Ωcm^2 (700°C), agreed well with the expected ohmic resistance of the 10-20 μm thick YSZ electrolyte. Each spectrum appeared to consist of a large higher-frequency depressed arc and a small lower-frequency arc, which both decreased in size with increasing temperature. The high-frequency arcs were larger for methane than for hydrogen, whereas the lower-frequency arcs appeared to change relatively little with fuel composition. The higher-frequency arc also changed with H_2 partial pressure (results not shown), suggesting that this arc was associated with the anode.

The following protocol was used to quantitatively determine the stability region. First, the cell was operated in hydrogen for more than 24 h to reduce the anode and fully stabilize the cell performance.



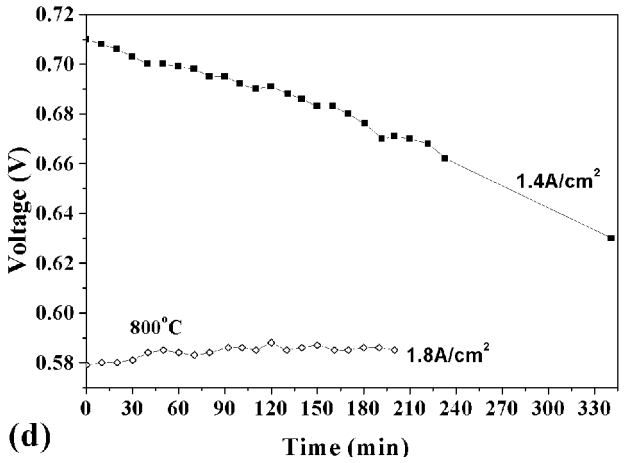


Figure 2. Cell Voltage versus Time at Constant Current J for SOFCs Operated in Humidified Methane at 700°C (a) and 800°C (b); the Cells Were Operated at Different *J* Values for 3-6 h in Each Step, Starting at High *J* and Reducing J in Steps

Second, the fuel was switched to methane with the cell maintained near the maximum power point. After the switch to methane, the *V* value at constant *J* dropped by ≈20% to a new steady-state value. The drop was expected based on the *I-V* curves in Figure 1. Third, *J* was maintained constant near the maximum power point for >3 h, long enough to observe whether *V* was stable. Fourth, *J* was reduced and maintained constant for >3 h. This latter step was repeated until *V* became unstable.

Figure 2 shows results taken in this way at 700 and 800°C. As shown in Figure 2a (700°C), stability in methane was excellent as long as a minimum cell current density $J \sim 0.1$ A/cm^2 was maintained. It was only at $J = 0$ that *V* decreased gradually over several hours. Thus, the critical current density J_c was $0<J_c<0.1$ A/cm^2 at these temperatures. The results were similar at 750 and 800°C (Figure 2b), but much larger critical current values, i.e. 0.8 A/cm^2 < J_c^{750} < 1.2 A/cm^2 and 1.4 A/cm^2 < J_c^{800} < 1.8 A/cm^2, were needed to maintain stable operation. These results imply that the SOFC oxygen ion current was at least partially responsible for preventing coking and thereby maintaining stable operation. We believe that J_c increased with increasing *T* because of the increasing rate of methane cracking above ≈700°C.[3]

Initial attempts have been made to examine the effect of methane concentration on stability. This is relevant to understanding SOFC operation in partially-reformed hydrocarbon fuels, where there will be significant amounts of methane present. In these initial experiments, the effect of methane concentration alone was examined (i.e. without introducing any other reforming species) by using a 50% methane - 50% Ar mixture. The results at 800°C showed that the cell was fairly stable except for $J = 0$, a remarkable improvement from the 800°C result in 100% methane (Figure 2b). This result indicates a surprisingly strong dependence on methane concentration. Further work is needed to fully characterize and understand this effect.

Mass spectrometer measurements of the anode exhaust gas were carried out to determine the nature of the anode reaction products. Figure 3 summarizes the product gas concentration results derived from the mass spectrometer data. Each of the species H_2, CO, CO_2, and H_2O increased with increasing *J*, but the increases in H_2 and CO were substantially larger. Note that an artifact in the mass spectrometer data, the so-called "zero blast" effect, caused the mass spectrometer to underestimate the size of low-mass peaks such as hydrogen. Thus, we believe that the hydrogen concentration should actually be larger than CO. Figure 3 is in reasonable agreement with thermodynamic calculations of the equilibrium anode exhaust gas composition.

Experiments were carried out testing the ability of ceramic anodes to withstand hydrogen-air and propane-air cycling. Figure 4 shows the result for propane-air cycling, with the cell maintained at a constant current of 200 mA/cm^2. The cell was

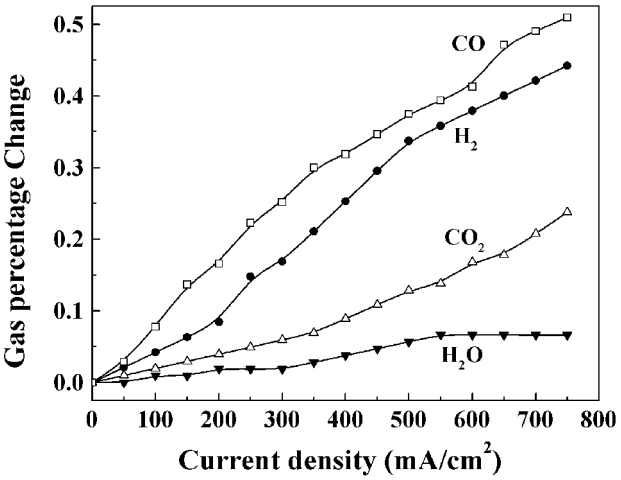


Figure 3. Changes in the Concentrations, in Percent, of Various Species versus SOFC Current Density during Operation in Humidified Methane at 800°C, Derived from Mass Spectrometer Data

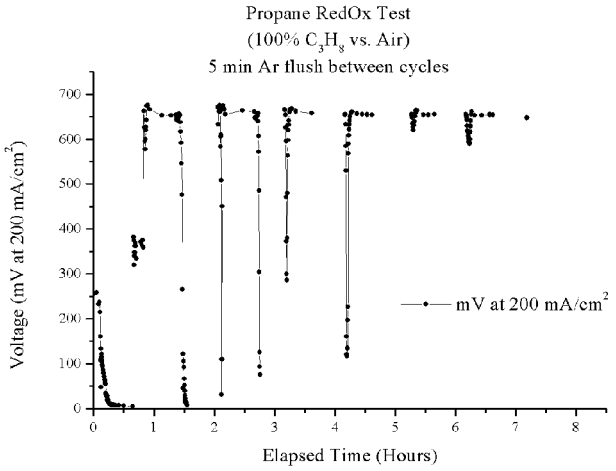


Figure 4. Propane-Air Redox Cycling Result for a Ceramic Anode SOFC

operated for ≈30 min in fuel, then the fuel flow was stopped and air allowed to enter the fuel compartment. The cell voltage and current rapidly dropped to zero. After ≈30 min, the fuel flow was re-started, whereupon the cell voltage and current rapidly returned to close to their original values. This cycle was repeated several times with similar results. Note that the transients at the beginning of fuel flow may be related to the time required to fully flush any air from the fuel lines. A total of 30 redox cycles were carried out during this cell test with no evidence of cell degradation. These results strongly indicated that ceramic-based anodes avoid problems with redox cycling.

Ni-YSZ anode-supported cell tests were carried out using H_2 fuel with 10 ppm H_2S. The cell test protocol was as follows: the cell was first run in dry pure H_2, then exposed to 10 ppm H_2S in H_2 during stable operation, and finally allowed to reach steady-state performance after returning to pure H_2. The effect of H_2S was minor at 700°C, but there was a substantial degradation at 800°C. This result is rather surprising based on prior results for 750-1000°C, suggesting that sulfur poisoning is exacerbated as the temperature is reduced.[4] More work is needed to understand this result.

Conclusions

Operation of Ni-YSZ anode-supported SOFCs directly on methane was studied, along with ceramic anode cells tested in a variety of hydrocarbon fuels. The results are beginning to provide a clearer picture of how these cells operate. The following are the main conclusions:

- Power densities as high as 0.5 W/cm^2 at 700°C and 1.2 W/cm^2 at 800°C have been achieved during direct methane operation. High open circuit voltages and large limiting currents are key reasons for the good performance in methane.
- The high-frequency impedance arc, probably associated with the anode, was substantially larger for methane than for hydrogen.
- The results suggest that SOFC performance is strongly dependent on gas diffusion and hence on anode parameters including thickness, porosity, and tortuosity.
- The SOFCs were stable without coking at $T \leq 700$°C, except at very low current densities. At higher temperatures, increasingly large currents were required to avoid coking and cell failure.
- Mass spectrometer measurements showed that H_2 and CO were the main reaction products, with H_2O and CO_2 minor products – all the products increased with increasing cell current density. While these results were in general agreement with thermodynamic predictions, the lack of coking during direct methane operation was not.

- The results suggest that coke-free SOFC operation was achieved due to kinetic limitations on the methane cracking reaction, particularly at low temperature. It is suggested that oxidation of hydrogen, produced by methane reforming by reaction products within the anode, is an important electrochemical reaction; the resulting steam helps remove solid carbon, thereby suppressing coking at high current densities. Detailed modeling of diffusion and reaction processes within the anode is needed.
- The ability of these cells to produce syngas (H_2 + CO) with simultaneous electrical power generation makes them interesting for low-cost production of hydrogen.

References

1. J. Liu, B. Madsen, and S.A. Barnett, Electrochem. Solid State Letters 5, (2002) A122.

2. S. Park, R.J. Gorte, and J.M. Vohs, Applied Catalysis A 200, (2000) 55-61.

3. C.M. Finnerty, N.J. Coe, R.H. Cunningham, and R.M. Ormerod, Catalysis Today 46, (1998) 137.

4. Y. Matsuzaki and I. Yasuda, In *Proc. 7th Int. Symp. On Solid Oxide Fuel Cells* (Yokokawa, H. and Singhal, S.C., Editors), Electrochem. Soc., p 769 (2001).

FY 2004 Publications/Presentations

1. A Atkinson, S Barnett, RJ Gorte, JTS Irvine, AJ McEvoy, MB Mogensen, S Singhal, J Vohs, "Advanced Anodes for High Temperature Fuel Cells," Nature Materials **3**, 17-27 (2004).

2. Yuanbo Lin, Zhongliang Zhan, Jiang Liu, and Scott Barnett, "Direct Operation of Solid Oxide Fuel Cells with Methane Fuel," Solid State Ionics, submitted.

3. Presentation at the SECA program review, Sacramento, CA, February, 2004.